Simulations of Surface Transfer Doping of Hydrogenated Diamond by MoO_3 metal oxide

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***Abstract*—In this work we investigate the surface transfer doping effect induced between hydrogen terminated diamond and MoO_3. We simulated the interface of (100) MoO_3 surface and hydrogen terminated (100) diamond surface using fist principle methods such as Density Functional Theory (DFT). DFT simulation allowed us to calculate the band structure and charge transfer between the MoO_3 and the diamond materials. Analysis of the band structures and density of states shows that the MoO_3 is an electron acceptor and injects holes into the diamond structure.**

Keywords-Surface transfer doping (STD); 2D hole gas (2DHG), diamond

I. Introduction

Diamond has unique properties that make it an attractive wide band-gap material to produce future high-performance electronic devices. With a wide band-gap of 5.5eV, a thermal conductivity 5 times greater than 4H-SiC of 24 W/cm*K (for CVD diamond), a high breakdown field of 20Wcm^{-1} and high hole and electron carrier velocities of 0.8x10^7cm/s and 2.0x10^7cm/s respectfully, diamond is a clear stand out candidate for high frequency and high power devices [1-3]. However, the lack of a suitable doping mechanism has hindered the application of diamond in electronic devices. Conventional substitutional doping is not an ideal option as it is difficult to substitute atoms into the diamond crystal lattice, limiting the potential for diamond to be used as a semiconductor in electronic applications [4]. It is possible to dope diamond with some atoms, boron being the most common. Boron doping has its limitations however - as the doping concentration is increased the hole mobility deteriorates and at doping concentrations above 3.9x$10^{21}$$cm^{-3}$ the diamond has semi metallic properties; at cryogenic temperatures it becomes superconducting [5]. Surface Transfer Doping (STD) gives the use of diamond for such applications more promise [6]. For STD to occur there are two prerequisites: hydrogen terminated diamond (H-diamond) and an electron accepting material in intimate contact with the H-diamond. The hydrogen termination gives the diamond a negative electron affinity which facilitates the transfer

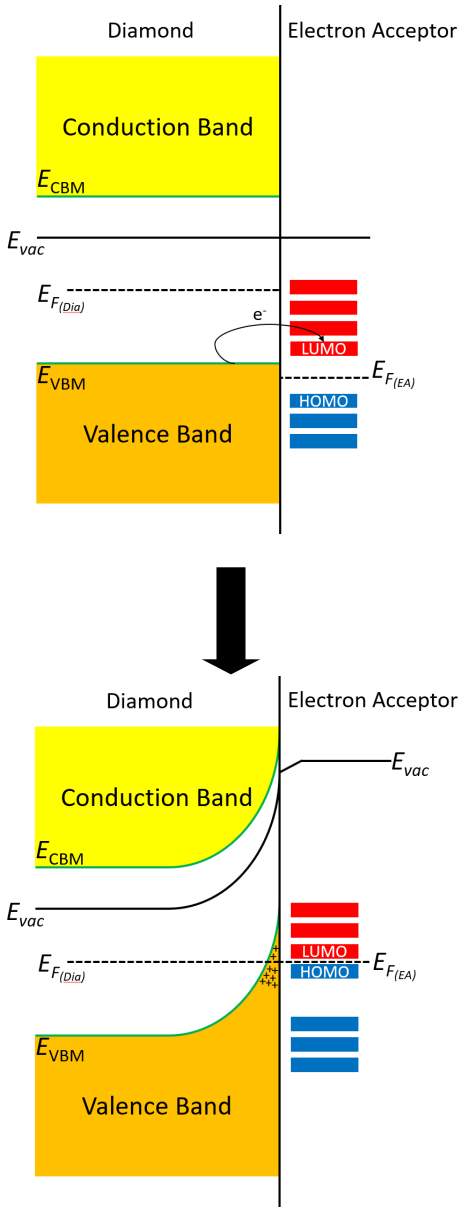

Figure 1. Band diagrams showing the interaction of hydrogen terminated diamond with a surface acceptor material.

of electrons from the diamond to the accepting material, creating a quasi two-dimensional hole gas (2DHG) in the diamond.

Figure 1 shows the band bending mechanism in the

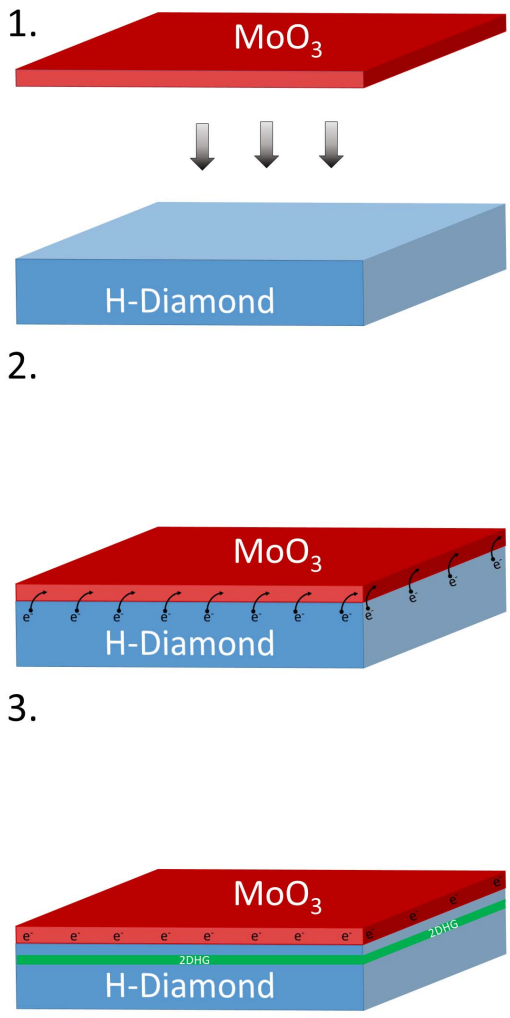

Figure 2. The creation of the 2DHG just below the diamond surface after interfaced with MoO_3.

H-diamond when it comes in contact with an electron acceptor. In the earliest developments of STD the accepting material was provided by molecules in the atmosphere spontaneously adsorbed onto the surface of hydrogen terminated diamond. However, the lack of control over the adsorption of these atmospheric molecules, and the fact they are readily desorbed by fabrication processes and raised temperatures, has led to research into alternative electron acceptors that can be controlled, are more stable and improve reliability [6].

One of the materials that has been experimentally proven to improve the performance and stability of STD is MoO_3 [7]. Figure 2 represents a schematic diagram which shows that when MoO_3 is deposited on H-diamond electrons from just below the surface of the diamond (~10nm) will transfer to the MoO_3 creating the 2DHG.

In order to investigate this hypothesis and mechanism in more detail, in this work we present Density Functional Theory (DFT) simulations investigating the processes of STD in diamonds. The theoretical study of the interface between the diamond and different oxides would help give a better understanding of the mechanisms at play and further develop knowledge in the field. Interfaces of (100) α-MoO_3 and 2x1-(100) H-diamond have been modelled and STD analysed. Establishing a high-performance STD process in the diamond will catalyse research in a wide area of diamond-based applications.

II. Simulation Methodology

All calculations were carried out with Quantumwise Atomistix ToolKit (ATK) software using DFT[8]. Generalised Gradient Approximation (GGA) exchange correlation was used for the geometry optimisations of all systems and GGA-1/2 exchange correlation was used for all electronic structure calculations. DFT method is well known for underestimating the bandgap of semiconductors [9], therefore to obtain a more accurate electronic description of the systems DFT-1/2 method was used. DFT-1/2 method is a semi-empirical approach which can overcome the error that local and semi-local exchange correlation density functionals inherently have when working with semiconductors and insulators. It works by correcting the self-interaction error of DFT by cancelling out the electron-hole self-interaction energy by defining an atomic self-energy potential [10]. However, DFT-1/2 method is not suitable for calculating properties that depend on total energy, hence, we used GGA for the geometry optimisations. Pardew, Burke and Ernzerhof (PBE) predefined functional was chosen for all calculations. A Monkhorst-Pack scheme with an 8 x 8 x 1 k-point density (Å) mesh was used for the Brillouin zone integration.

The H-diamond and MoO_3 were created and geometry optimised individually. The (100) MoO_3 was then interfaced with 2x1-(100) H-diamond with a strain of <1% being placed on the MoO_3. To optimise the interface separation the H-diamond was fixed and the MoO_3 atoms were rigid for the geometry optimisation calculation. The interface distance was corrected for counterpoise basis set superposition error and van der Waals interactions.

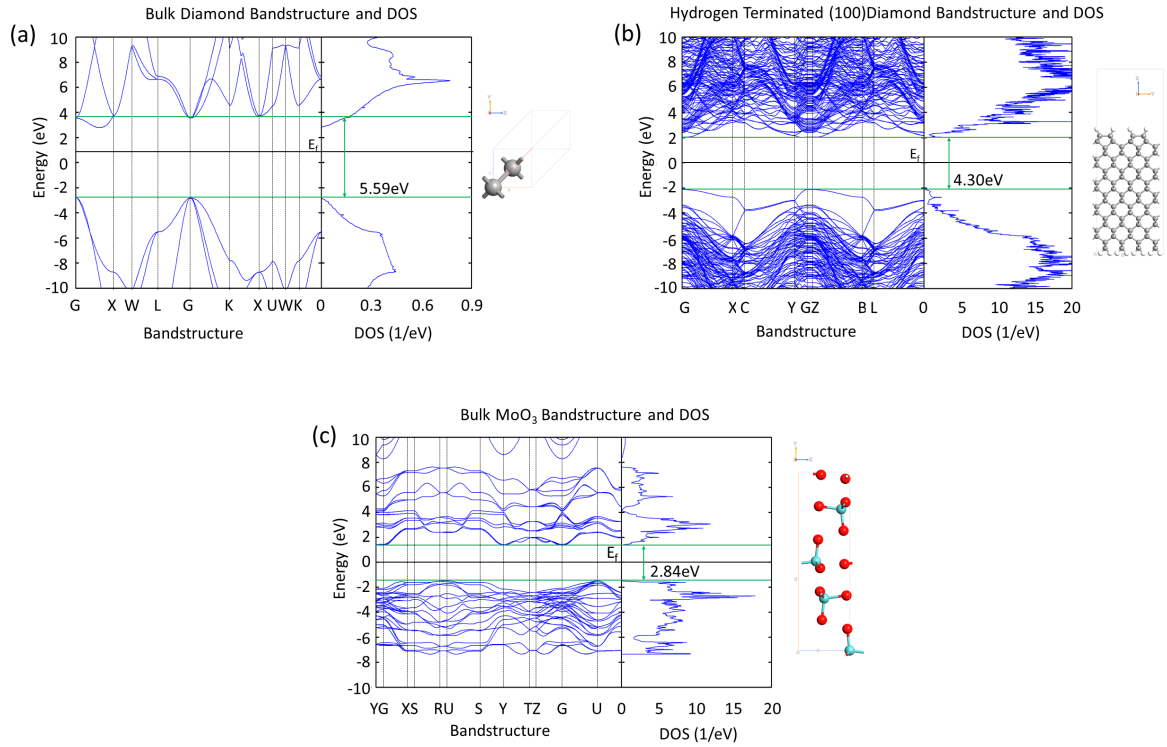

Figure 3. (a) bandstructure and DOS of bulk diamond showing a band gap of 5.59eV, (b) bandstructure and DOS of hydrogen terminated (100) diamond shoing a reduced band gap of 4.30eV, (c) bandstructure and DOS of bulk MoO_3 showing a band gap of 2.84eV.

III. Results and Discussion

Fig. 3 compares diamond, hydrogen terminated diamond and MoO_3 band structure and DOS obtained from the super cell DFT simulations. The data presented in Fig 3 (a) and (b) shows that when diamond is hydrogen terminated the band gap is slightly reduced at the surface due to surface gap states at the valance band maximum (VBM) because of the presence of hydrogen atoms. Although the band gap has been reduced to 4.30eV when the DOS is projected for carbon atoms in the bulk of the structure the band gap remains ~5.5eV.

The band gap of 2.84eV obtained for MoO_3 (Fig 3(c)) is comparable to reported experimental values between 2.9-3.15eV [11]. MoO_3 is an amorphous material and therefore does not have a well-defined crystal structure. In our simulations the MoO_3 is built as a perfect crystal and this is the reason that the band gap obtained from the DFT is slightly lower that the reported experimental results.

Figure 4 shows the Projected Density of States (PDOS) for the 's' electron shells of the hydrogen and the 'p' electron shells of the carbon atoms before and after the H-diamond has been interfaced with MoO_3. The PDOS diagram reveals that when the H-diamond

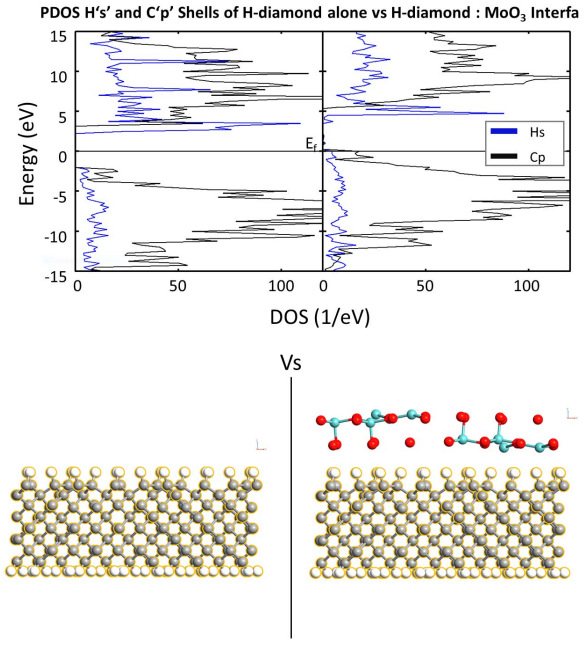

Figure 4. PDOS plots of Hs and Cs shells before and after the H-diamond is interfaced with the oxide. The lower image shows the repeating units of the systems with the atoms highlighted that are being projected in the PDOS plot.

is in contact with the metal oxide there is a shift of the PDOS to higher energies and the Fermi Level (E_F) is in contact with the valence states. The band gap of the diamond remains constant but the VBM has moved closer to the E_F as it crosses the fermi level, which in turn means the conduction band minimum (CBM) also moves upwards, indicating that there has been charge transfer at the interface.

The PDOS plot of the H_s, C_p and Mo_d shells in Figure 5 shows that the Mo_d has states that lie within the bandgap of the diamond and can accept electrons. Hence, this result suggests electrons transfer from the diamond to the oxide creating 2DHG in the diamond surface which is in direct contact with the metal oxide.

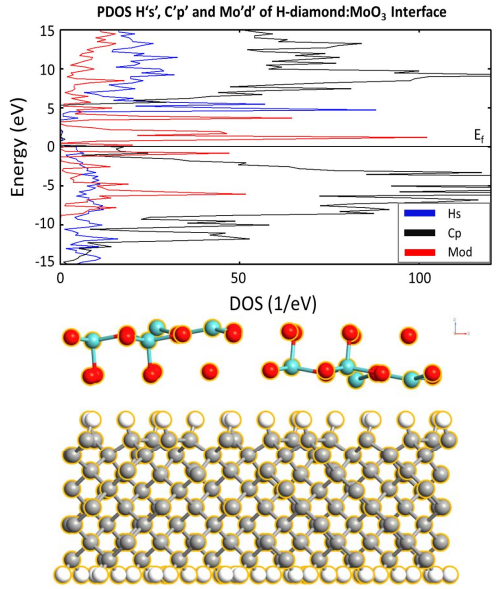

Figure 5. PDOS plot of Hs, Cs, and Mod shells when the interface is created with the image of the repeating unit of the system below.

Analysis of the Mulliken electron population of the system showed that there was a transfer of 3.6 electrons from the H-diamond to the oxide. Given that the surface area of the system was ~60Åx10Å this would mean that calculating the charge transfer per cm^2 would be ~$6x10^{13}cm^{-2}$. This is comparable to reported experimental values obtained by hall measurements of MoO_3 deposited on the surface of H-diamond substrates of ~$2.5x10^{13}$ – $6x10^{13}cm^{-2}$ carrier concentration [12].

Element	Mulliken Electron Population	
	Isolated element	Average per Atom After Interfaced
C	4	3.5804
H	1	1.3732
Mo	12	12.0097
O	6	6.7141

Table 1. Showing the change in electron population per atom.

Table 1 shows that the average electron population of the carbon atoms in the interfaced system decreased but, the average electron population of the hydrogen, molybdenum and oxygen atoms increased which is due to the charge transfer from the diamond through the hydrogen atoms to the MoO_3. It also suggests that the majority of the charge transfer goes to the oxygen.

IV. Conclusion

In this work we investigated the surface transfer doping effect induced between hydrogen terminated diamond and MoO_3. We simulated the interfaces of (100) MoO_3 and hydrogen terminated (100) diamond using DFT calculations. The PDOS data shows there is shift of the VBM and CBM bands of the H-diamond and there is charge transfer between the diamond and the metal oxide. The oxide readily acts as an electron acceptor to the diamond and creates a 2DHG in the diamond. The carrier concentration in the diamond has been calculated to be $6x10^{13}cm^{-2}$ which is similar to experimental values of single crystal H-diamond substrates with a deposited layer of MoO_3.

References

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